GENERAL DYNAMICS | CONVAIR

Report No. 8926-101

Material - Ceramics - Ceramic Fiber - Ceramic Matrix Systems

J. E. Shoffner, E. E. Keller, W. M. Sutherland

27 October 1959

Published and Distributed
under
Contract AF 33(657)-8926

Post Office Box 1950, San Diego 12, California CYpress 6-6611
Material Post Office Box 2071 BRoadway 3-8000 | Accounting Post Office Box 510

Report No. 8926-101

Material - Ceramics - Ceramic Fiber - Ceramic Matrix Systems

Abstract

Recent trends in fiber development, research topics initiated, facilities for fiber production, fiber testing techniques, and an initial composite ring specimen preparation are discussed.

Reference: Shoffner, J. E., Keller, E. E., Sutherland, W. M., "Ceramic Fiber - Ceramic Matrix Systems," General Dynamics/Convair Report MP 59-086, San Diego, California, 27 October 1959. (Reference attached).

CONVAIR
A DIVISION OF GENERAL DYNAMICS CORPORATION
SAN DIEGO

STRUCTURES-MATERIALS LABORATORIES

REPORT MP-59-086
DATE 27 October 1959
MODEL REA-8009

TITLE

REPORT NO. MP-59-086

CERAMIC MATRIX-CERAMIC FIBER

COMPOSITE SYSTEMS

REA-8009

PREPARED BY J. E. Shoffner
J. E. Shoffner

GROUP Materials and Processes Laboratories

CHECKED BY: E. E. Keller
E. E. Keller

REFERENCE MP-58-148.2

CHECKED BY W. M. Sutherland
W. M. Sutherland
Group Engineer

APPROVED BY E. F. Strong
E. F. Strong, Chief
Structures & Materials Laboratories

NO. OF PAGES 27

NO. OF DIAGRAMS 11

REVISIONS

NO.	DATE	BY	CHANGE	PAGES AFFECTED

FORM 1812A-4
ccl

RECOMMENDATION:

Initial investigations have shown the desirability of continuing studies of ceramic-fiber- - ceramic-matrix systems. The project should, however, be divided into (a) fundamental fiber studies, and (b) composite studies using existing material combinations. For the studies to be fruitful, long term funding and additional equipment is required.

INTRODUCTION AND RECENT TRENDS:

Report No. MP-58-148.2 (31) presented the desirable features of fiber composite systems. The need was stressed for more detailed technical information on the refractory fibers which have been reported, and the requirements of more refractory fibers than typical "E" glass.

This report covers the recent trends in fiber development, research topics initiated by this investigation, the establishment of facilities for fiber production, fiber testing techniques, and initial composite ring specimen preparation.

Horizons (17) has now released information on "non-glassy ceramic materials." Emphasis has been placed on alumina and zirconia fibers but a variety of oxides and oxide compounds are anticipated. The fibers are relatively short, from a fraction of an inch to about three inches. The zirconia fibers vary from 3 to 30 microns in diameter and the alumina fibers are approximately one micron in diameter. The strength of the fibers is reported to be comparable to soft glass but this, the author believes, is doubtful. The process for making these fibers was not disclosed. On a trip to Boeing Aircraft Company it was disclosed that the fibers are grown from a solution and then sintered.

Bjorksten (1) Laboratories are working with refractory inclusions in fibers. Although the idea appears promising, the results indicate that more extensive work is required.

Fiber composite systems are now actively being pursued by many laboratories.

GENERAL EQUIPMENT REQUIREMENTS FOR FIBER PRODUCTION:

The two methods normally used in making continuous fibers are described below.

a) Rod Method

The rod of fused or sintered material is heated on the end until the tip melts and falls by its own weight. The feed of the rod is started at this time. The advantage of this method is the elimination of a container for the melt. The disadvantages are as follow:

GENERAL EQUIPMENT REQUIREMENTS FOR FIBER PRODUCTION: (Continued)

a) Rod Method (Continued)

1) Requires controlled rod feed.
2) Requires closely controlled draw rate.
3) The production of rods adds an extra step in the process.
4) The method is not as adaptable to production - - multifilament drawing techniques

b) Bushing Method

A platinum, crucible (called a bushing) with one or more orifices in the bottom is heated until the fiber forming material melts. Beads of the melt at the orifice are caught and pulled into fibers.

The principal disadvantage, for the more refractory melts, is the requirement of bushing material to withstand oxidation and the attack of batch materials. Tantalum, molybdenum, and tungsten (11) have been investigated as crucibles, using controlled atmospheres, but with limited success.

Using either the rod or bushing method, the fibers are attached to a revolving variable speed take-up drum.

HEAT SOURCE REQUIREMENTS:

Table I lists the heat sources considered versus the anticipated requirements for fiber production. The section on laboratory investigation covers in detail the tests performed and equipment evaluated. Induction heating was selected for major emphasis for the following reasons:

1) Unit was available.
2) Most flexible in equipment design and operation.
3) Unit was easily adapted for controlled atmospheres.

ACCESS NO.

Title: MATERIAL - CERAMICS - CERAMIC FIBER - CERAMIC MATRIX SYSTEMS.

Authors: Shoffner, J. E., Keller, E. E., Sutherland, W. M.
Report No: 8926-101 Date: 27 October 1959
Contract: R.E.A. 8009
Contractor: General Dynamics/Convair
ABSTRACT: Recent trends in fiber development, research topics initiated, facilities for fiber production, fiber testing techniques, and an initial composite ring specimen preparation are discussed.

27 pages, 2 tables, 10 figures.

TABLE I HEAT SOURCES

REQUIREMENT	INDUCTION	RESISTANCE	ELECTRON GUN	ELECTRIC ARC	CARBON ARC IMAGE	SOLAR ENERGY	COMBUSTION GASES	GLOW DISCHARGE
2300 - 3200°C	✓	✓	✓	✓	✓	✓	D	✓
REQUIRES VACUUM OR INERT GAS	✓	✓	✓					✓
QUANTITY OF HEAT	✓	✓	✓	✓	?	?	✓	✓
CONTROL OF RATE	✓	✓	✓	D	✓	✓	D	?
FOCUS HEAT	D	D	✓	✓	✓	✓	D	✓
ABSENCE OF TURBULENCE	✓	✓	✓	✗	✓	✓	✗	✓
UNIFORMITY OF HEAT	✓	✓	D	D	D	D	D	✓

✓ = SATISFACTORY
✗ = UNSATISFACTORY
D = DIFFICULT

MATERIAL CONSIDERATIONS:

The materials selected for study were alumina, high aluminum silicates, zircon, and zirconia. No known evidence exists of the pure oxides being present in the non-crystalline or amorphous state. Calcium aluminate glasses have been made, but many other oxides were present. The materials studied are refractory, available in rod form, and have a range of physical, electrical, and thermal properties of interest for the composite systems.

Two approaches for forming amorphous alumina containing materials were suggested as follow:

1) Gradually decrease the silica content in alumina-silica systems to the point at which glasses could not be formed.

2) A unique system by which the molten alumina (low viscosity) could be quenched at a rapid enough rate to form the non-crystalline state.

The first approach can be handled using the rod method of producing fibers or the crucible method, providing container materials are available.

Flash heating is suggested as a unique means of investigating which amorphous compositions can be made. Using crystalline fibers of alumina or zirconia and the light source developed by Bell Laboratories, (27) filaments are suspended in a transparent medium and exposed to a high intensity, high speed flash heating. The time elapse between heating and quenching is in the order of a few milliseconds.

The equipment described uses capacitances as high as 1296 microfarads charged to 4KV. The maximum temperature is reached in the 1 to 100 micron wave length and in a vacuum. The temperature is limited by black body re-radiation - approximately 5000°C. Tungsten wire has been vaporized and glass fibers heated using this technique.

Materials Used

The rods used in the experiments performed were alumina, zircon, and zirconia produced by Norton Co. for flame spray application. The production of rods of varying compositions is a project in itself. Figure 1, on the next page, illustrates an extrusion die design for producing rods. The density, tolerances (variations of diameter and straightness) and other physical properties of the rods are very important in the close controls necessary to produce fibers.

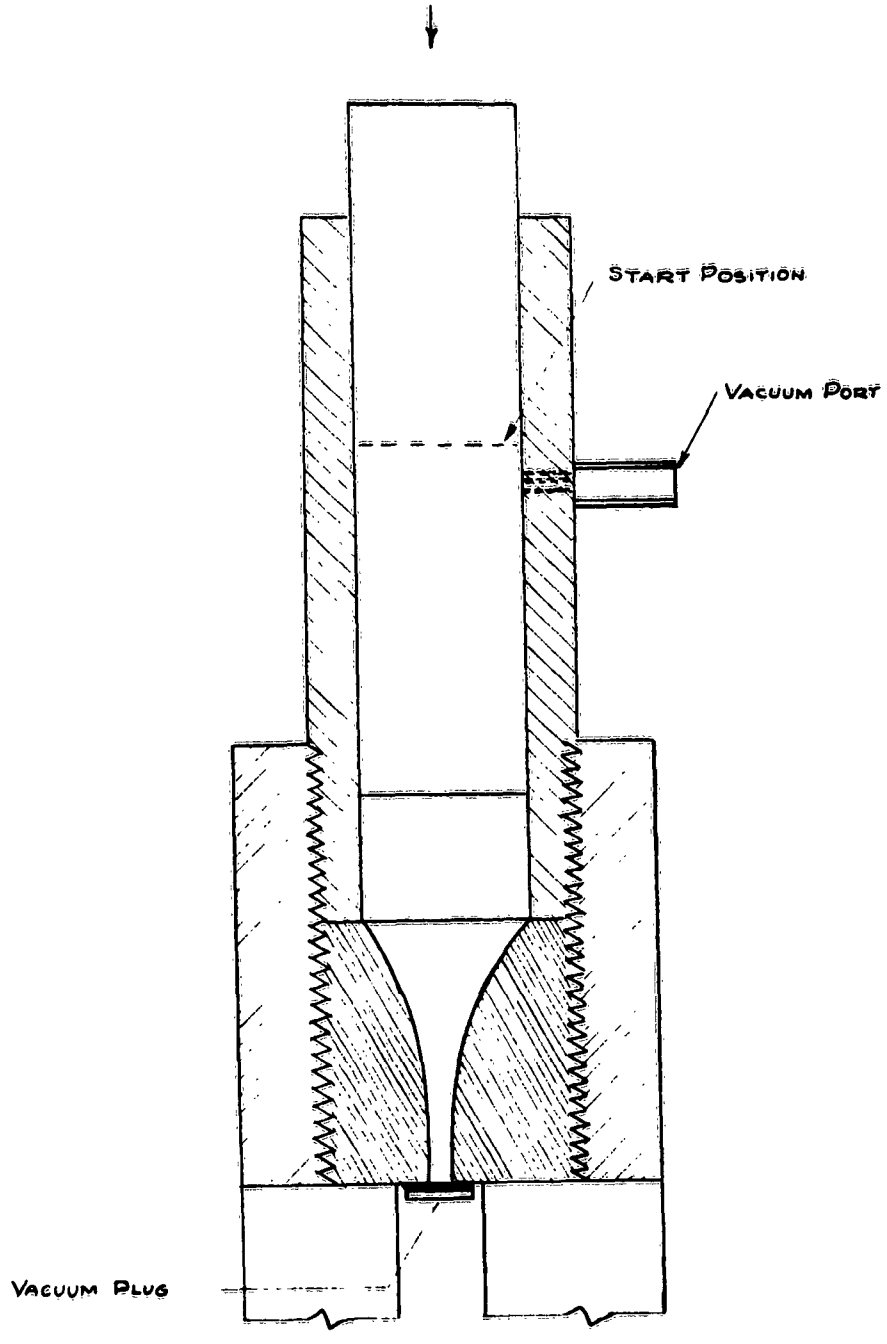


FIGURE 1
EXTRUSION DIE

NATURE OF VISCOSITY OF GLASS:

In processing glass, from the melt through the strain point, viscosity is of prime importance. Before discussing the theory of viscosity, a brief review of the practical terminology is in order. Figure 2 shows the viscosity temperature curves of several glass compositions. In the molten state, the log viscosity (poises) is approximately 2. On cooling, the working range is defined as the temperature range at which the log viscosity is 4. At the softening point, the temperature at which a piece will deform under its own weight, the log viscosity is defined as 7.6.

On cooling further the annealing point, the temperature at which internal strains are rapidly removed, is reached at a log viscosity of 13.4. And finally, the strain point, the temperature where no permanent internal strains can be induced by thermal gradient, is reached at a log viscosity of 14.6.

Model for Viscosity

Eyring (16) regards a liquid as holes moving in matter - - glasses have been defined as supercooled liquids. The energy required to make a hole of molecular size in a liquid is thus equal to the energy of vaporization per molecule of the latter. The activation energy for viscous flow may be regarded as consisting of two parts, the energy to form a hole and the energy required for the molecules to move into the hole.

For Newtonian flow, no change in viscosity with rate of shear, Eyring's formula given below can predict viscosity (η) within less than 30 percent.

$$\eta = \frac{hN}{V} e^{\Delta E_{VAP}/2.46RT}$$

h = Planck's Constant
N = Avogadro's Number
V = Molar Volume
R = Gas Constant
T = Temperature (°K)
E = Energy of Vaporization

This formula applies for low shear values, (less than 10^8 or 10^9 dyne/$_{cm^2}$).

For non-Newtonian flow, the following formula has been proposed:

$$\eta = A f e^{(a-bf)/T}$$

The shear values ^{f} above 10^9 dynes/cm^2

A, a, & b, = constants
f = shear force dynes/cm^2

Eyring stated that glasses obey non-Newtonian flow. Bockris,[7] however, stated that several systems investigated obeyed Newtonian flow.

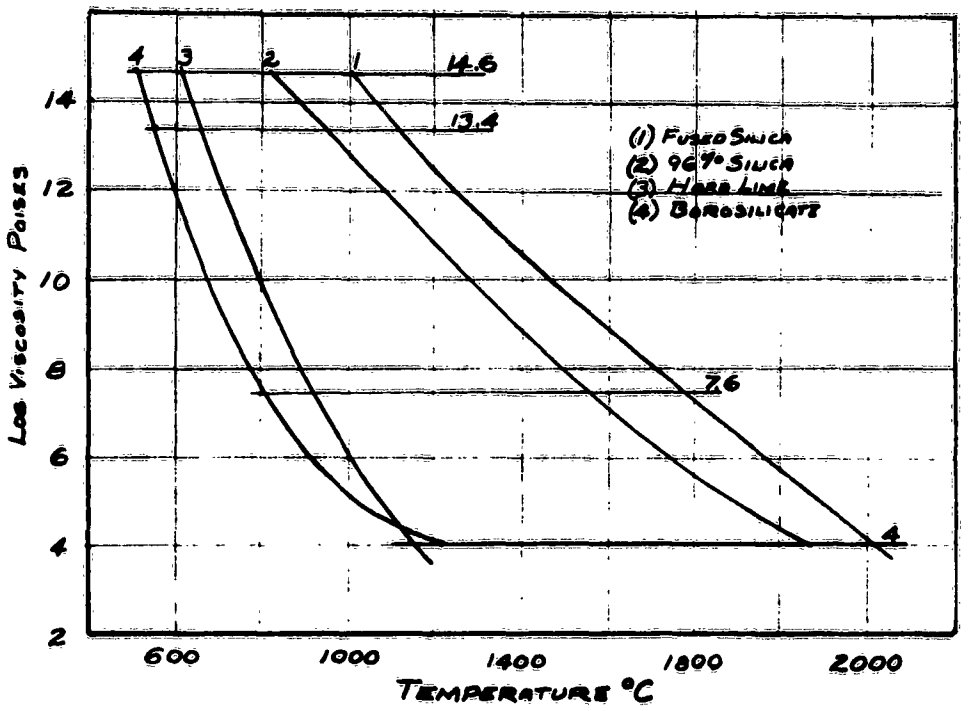


FIGURE 2

VISCOSITY-TEMPERATURE CURVES

REFERENCE #9

NATURE OF VISCOSITY OF GLASS: (Continued)

Good (15) calculated the viscosity shearing force curves (Figure 3) using data of Bockris. The graph shows that the viscosity decreases rapidly above a critical value. For a change of a factor of 4 in the shear force, the viscosity decreases by a factor of 100. If a high shear force is applied, the temperature for a given viscosity decreases. At a shear force of 14×10^9 dynes/cm^2, the viscosity at 1345° F. is equal to the viscosity at 2256° F.

Good concludes that the theory requires more extensive verification in the glass field, and that the force is dependent on the molecular unit of flow which has not been adequately defined.

$Si_3O_9^{6-}$ rings, $Si_4O_{10}^{4-}$ tetrahedral units, and a combination of these have been proposed as the molecular units. Mackenzie (22) proposes the planar rings as the discrete units, as shown in Table II. Bockris (6) proposes SiO_4^{4-} units for ortho-silicate compositions, rings or infinite chains $Si_nO_{3n}^{2n-}$ as the silica content increases, extension of two dimensional sheets of $Si_{2n}O_{5n}^{2n-}$ at 33.3 mole percent metal oxide (mo), and increasing three dimensional bonding as the SiO_2 content is further increased.

The more refractory compositions under consideration have not been investigated. The understanding of the viscosity shear relationship is a fundamental requirement for further fiber studies.

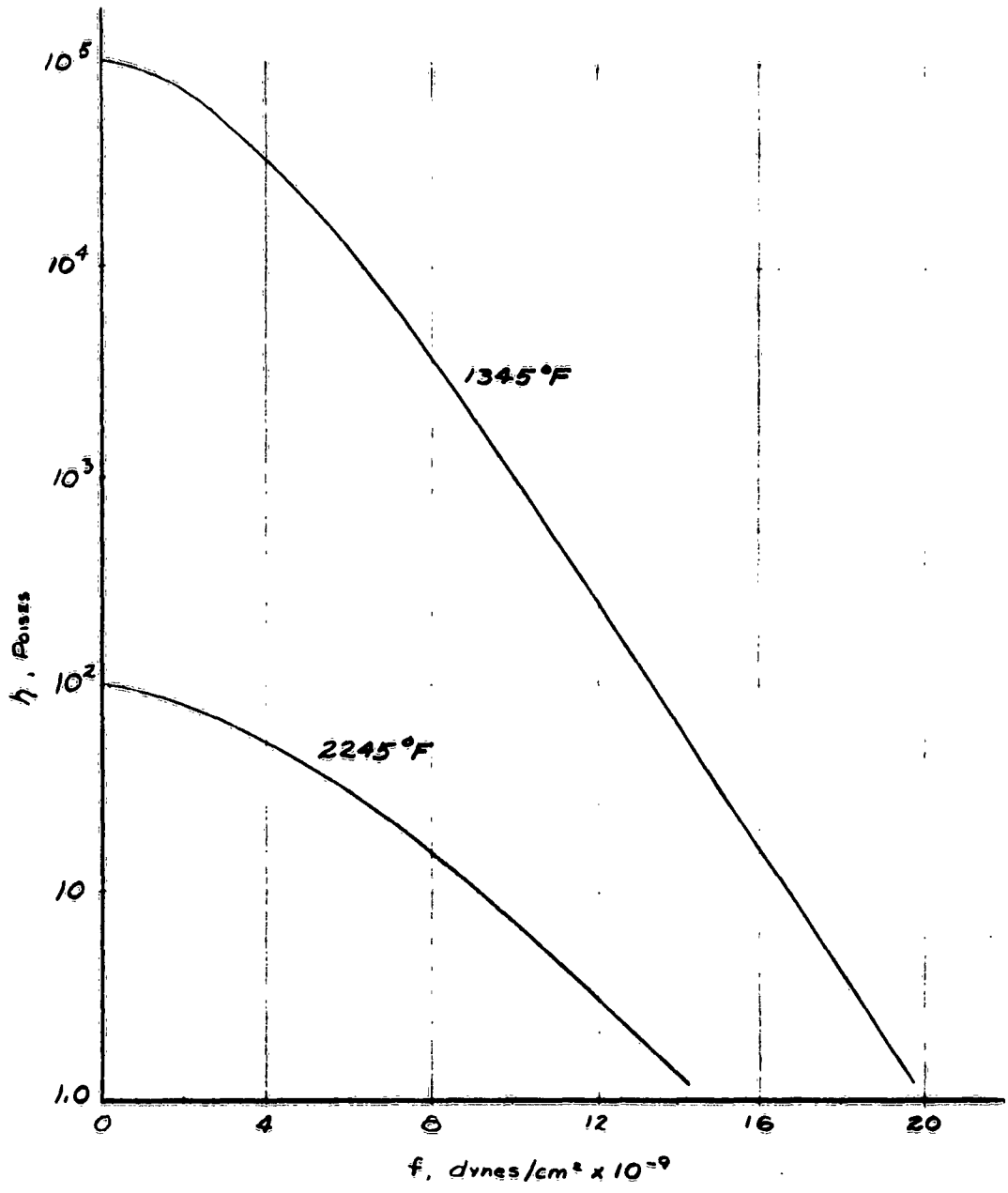


FIGURE 3

NON-NEWTONIAN, VISCOSITY
AS FUNCTION OF SHEARING FORCE

REFERENCE #15

CONVAIR
SAN DIEGO

FORM 73-1

TABLE II MOLECULAR UNITS

	Melt Composition	Mole Per Cent	Discrete Ion	Chain Length A
	SiO_2:MO	50	$Si_2O_6^{6-}$	—
2	SiO_2:MO	33	$Si_6O_{15}^{6-}$	6
3	SiO_2:MO	25	$Si_9O_{21}^{6-}$	9
4	SiO_2:MO	20	$Si_{12}O_{27}^{6-}$	12
5	SiO_2:MO	16.7	$Si_{15}O_{33}^{6-}$	15
6	SiO_2:MO	14.3	$Si_{18}O_{39}^{6-}$	18
7	SiO_2:MO	12.5	$Si_{21}O_{45}^{6-}$	21
8	SiO_2:MO	11.1	$Si_{24}O_{51}^{6-}$	23

REFERENCE #7

NATURE OF FIBERS:

Additional emphasis is again placed on the difference between fibers (non-crystalline, 5.8 - 19.1 micron diameter) and bulk glass. The extremely rapid chilling rate of 10,000°F/sec. lowers the density, modulus of elasticity and index of refraction of the fibers as compared to bulk glass. The fibers are further from equilibrium condition, or represent more of the high temperature structural configuration. When a fiber is reheated after forming, the properties change to values representative of the massive form. The increase in density, called thermal compaction by Otto(28), could be interpreted as a collapse of the holes put in to produce the viscosity of the molten glass. The holes or random structure is frozen when the glass is quenched.

Crystalline solids have a melting point while glasses have a transition range which normally falls between 400 to 600°C. To describe the thermal history of glass in this range, the term, "fictive temperature", was developed which is defined as follows:

> For temperatures T, below transformation range, the material is said to have a fictive τ (Tau) if it is in the state produced by rapid quenching from complete equilibrium at temperature $T = \tau$. The state is usually characterized by a measurable physical property. The transformation range is established because an upper limit is set - - quenching occurs at a finite rate; and, the lower limit is set because as the temperature is lowered, a longer time is required for equilibrium. Figure 4 illustrates the differences in thermal expansion of annealed bulk glass, chilled bulk glass and fibers.

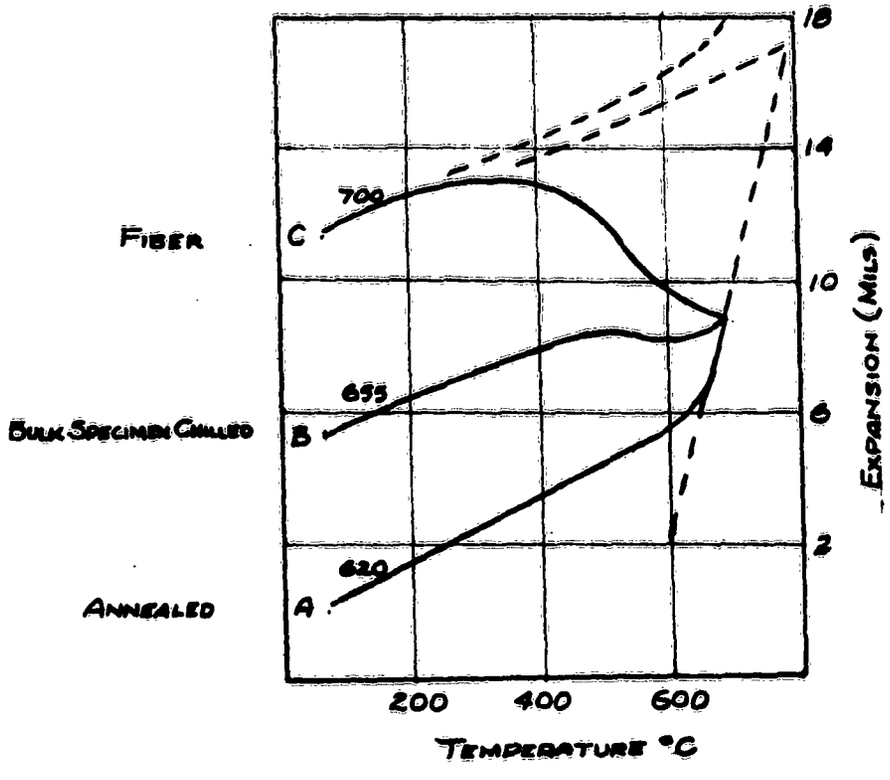


FIGURE 4

EXPANSION CURVE, BOROSILICATE GLASS

REFERENCE #9

TESTING OF FIBERS:

In testing fibers, the differences in bulk glass and fibers must be considered as the results vary widely with test conditions. Otto's (28) excellent work emphasizes this point. Figure 5 illustrates the effect of heat treatment on the modulus of elasticity of fibers.

On a recent field trip to Owens Corning Fiberglas Research Center, Otto demonstrated equipment which appears to be the ultimate in simplicity in testing techniques. The majority of investigators use commercial testing units which limit the number of specimens tested or increase the cost. Otto's unit was designed to test 8 fibers simultaneously. The loading jaw is driven by a constant speed motor through a gear reducer to provide a rate of strain of 0.063 in/in/min. for a gage length of 2.5 inches. The load cells are the simple cantilever beam type employing linear variable differential transformers (LVDT) as the sensing elements. The transformers are powered at 8,000 cycles/sec and the output fed to an 8-channel recording oscillograph (Minneapolis-Honeywell Visicorder). For static fatigue, the fibers are secured on fixed jaws and on pivoted jaws at which point the fiber is loaded (lead weights) with mercury switches to a timer. Split furnaces are used with the above units for elevated temperature testing. The above equipment approach is recommended for required testing.

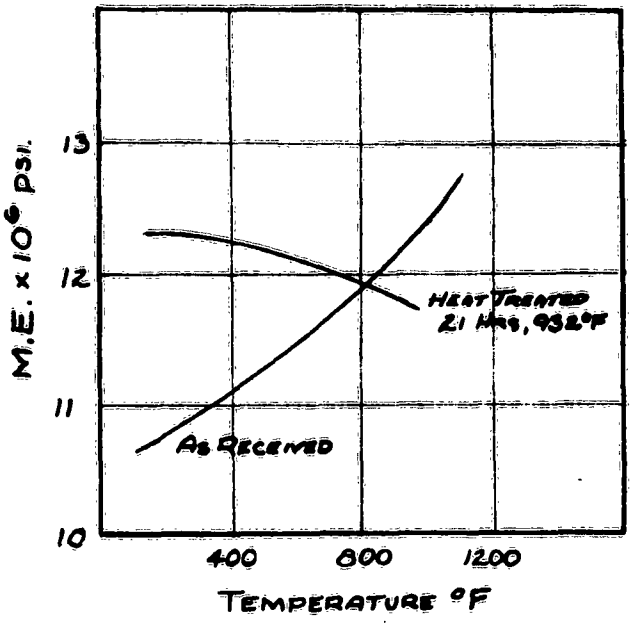


FIGURE 5

MODULUS OF ELASTICITY
VS. TEMPERATURE, "E" GLASS

REFERENCE #28

EFFECT OF PARTICLE SIZE ON MELTING:

Horizon (31) used colloidal silica as their matrix material. The size of Ludor colloidal silica was reported as 10-30 millimicrons. Galli (13) stated that small particles melt at lower temperatures than bulk materials and developed formulas for calculating the lowering of melting point. Bickerman (5) states that, "At the melting point, the vapor pressure of the solid is equal to that of the liquid. If the vapor pressure of small crystals is greater than that of large crystals, it is equal to that of the liquid at a lower temperature than the melting temperature of the bulk solid; hence, small crystals should melt at a lower temperature than large ones."

The use of colloidal size material to build up a shape provides a most interesting approach and is believed to be influenced by the above theories. Additional research work is suggested to cover this area.

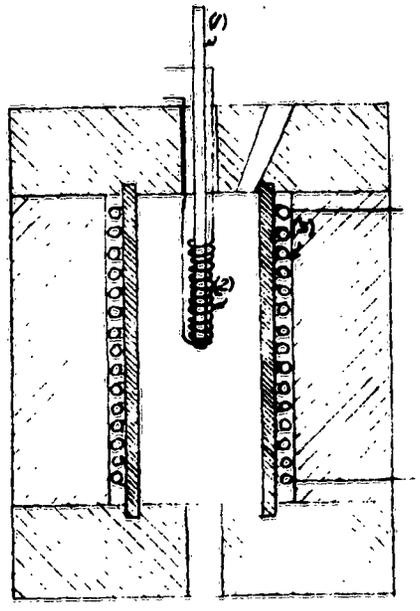
LABORATORY PROCEDURES:

Preliminary Heat Source Evaluation

The following preliminary heat source evaluation tests were performed in the vacuum coating unit at pressures less than 10^{-5} mm Hg.

a) Resistance heating

A coil of tungsten wire was used as shown in the sketch below.



(1) Al_2O_3 Rod
(2) Main Resistance Unit Tungsten
(3) Guard Heater

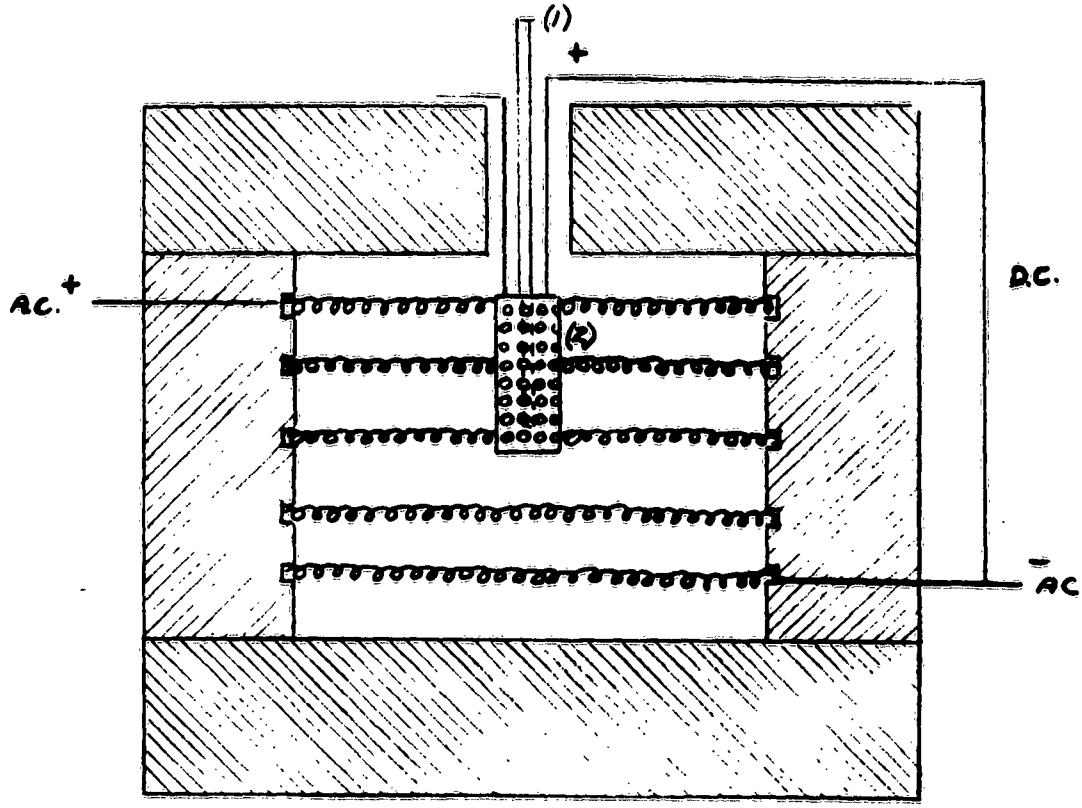
Preliminary Heat Source Evaluation (Continued)

a) Resistance heating (Cont'd)

The power supply was not adequate, the alumina volatilized, and the vacuum tank heated excessively. The tests were therefore discontinued.

b) Glow Discharge Unit

The test unit shown below was constructed. The heater coils were coated with barium and strontium oxides as emitters. The feasibility of this approach was established but test difficulties indicated that this line of investigation be dropped.



1. Al_2O_3 Rod
2. Molybdenum Screen

Preliminary Heat Source Evaluation (Continued)

c) Induction Heating

A 2.5 KW vacuum tube induction heating unit was used. The metal susceptor was not thermally insulated and the power supply was inadequate. With an insulated system the unit could be used.

Summary

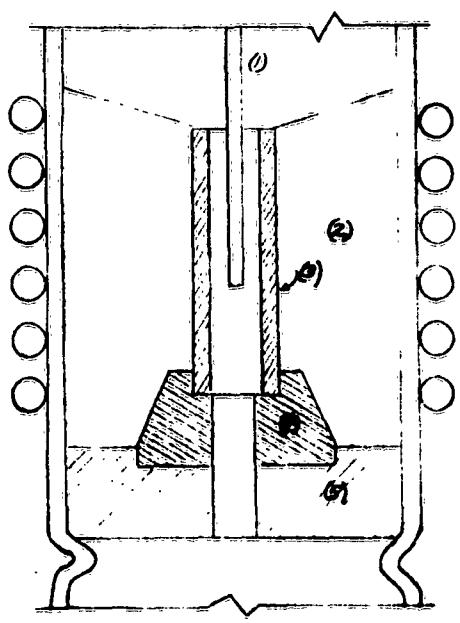
The use of a relatively large vacuum chamber with extended pump down time indicated the use of inert gas systems unless better vacuum facilities were obtained.

Inducting Heating Facility

The Lepel, Spark-Gap, 15 KW output unit was used in this investigation. Temperatures were measured with an optical pyrometer and controlled with step power settings, tuning, and an off-on foot switch. The following experiments were performed to evaluate susceptor design.

a) Graphite Tube

Using a graphite tube as sketched below and alumina rods, aluminum carbide was formed which penetrated the extrusion planes of the alumina rod which prevented proper melting conditions.



1. Al_2O_3 Rod
2. ZrO_2 Insulating Grain
3. Graphite Susceptor
4. Al_2O_3 Castable
5. Insulating Refractory

Inducting Heating Facility (Continued)

b) Molybdenum Tube

Using a molybdenum tube susceptor with or without radiation shields, the temperature fluctuated excessively with the off-on control.

c) Molybdenum Tube with Graphite Ring and Insulation

Figure 6 illustrates the system which proved the most successful. It was adopted for further tests and is discussed in detail in the next section.

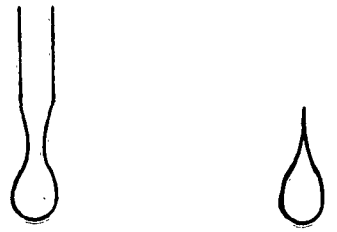
Fiber Unit Operation

Figures 6, 7 and 8 show the induction heating unit as dictated by previous experiments. The following steps were employed in its operation:

1) The proper power setting for a given susceptor was selected that would, with a minimum flow of argon and the foot switch on continuously, reach the desired temperature. The unit was turned off peak frequency, if lower power input to the susceptor was required.

2) The rod was inserted so that the tip was in the hot zone and an excess of argon was flushed through the chamber.

3) After the temperature became constant, the flow of argon was slowly reduced and the temperature brought to the desired value. Using alumina rods and temperatures of 2200°C, a bulb was formed which had a necked cross section above the bulb. (Sketch "A" below) The next, most critical, step of gradually lowering the bulb further into the hot zone could not be manually accomplished. The rod would be lowered too rapidly, the necked section would become too fluid, and the bulb would drop. (Sketch "B" below)



(A) (B)

FIGURE 8.

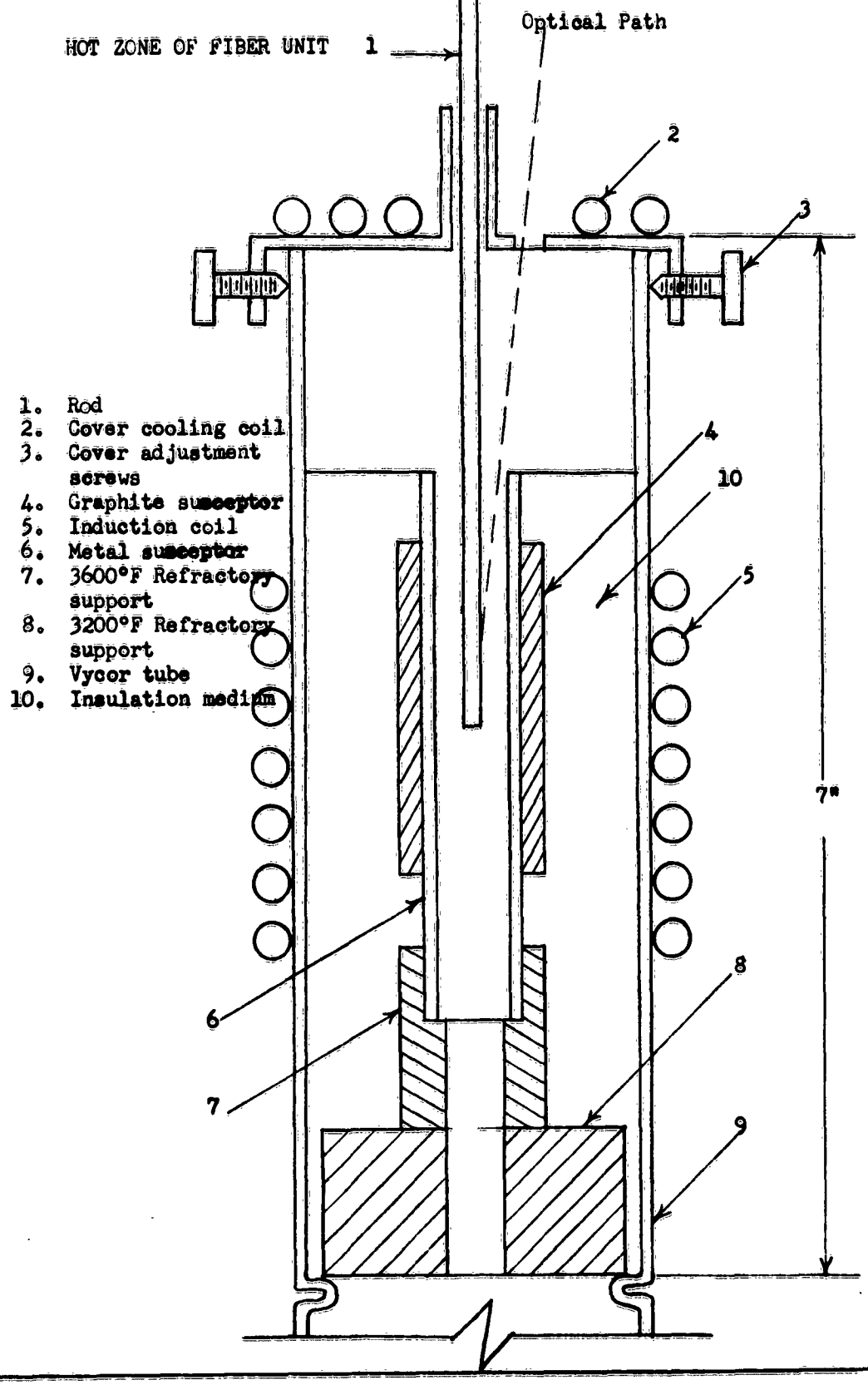

HOT ZONE OF FIBER UNIT 1
Optical Path
1. Rod
2. Cover cooling coil
3. Cover adjustment screws
4. Graphite susceptor
5. Induction coil
6. Metal susceptor
7. 3600°F Refractory support
8. 3200°F Refractory support
9. Vycor tube
10. Insulation medium
2
3
4
10
5
7"
6
8
7
9

Figure 6
Fiber Drawing Unit

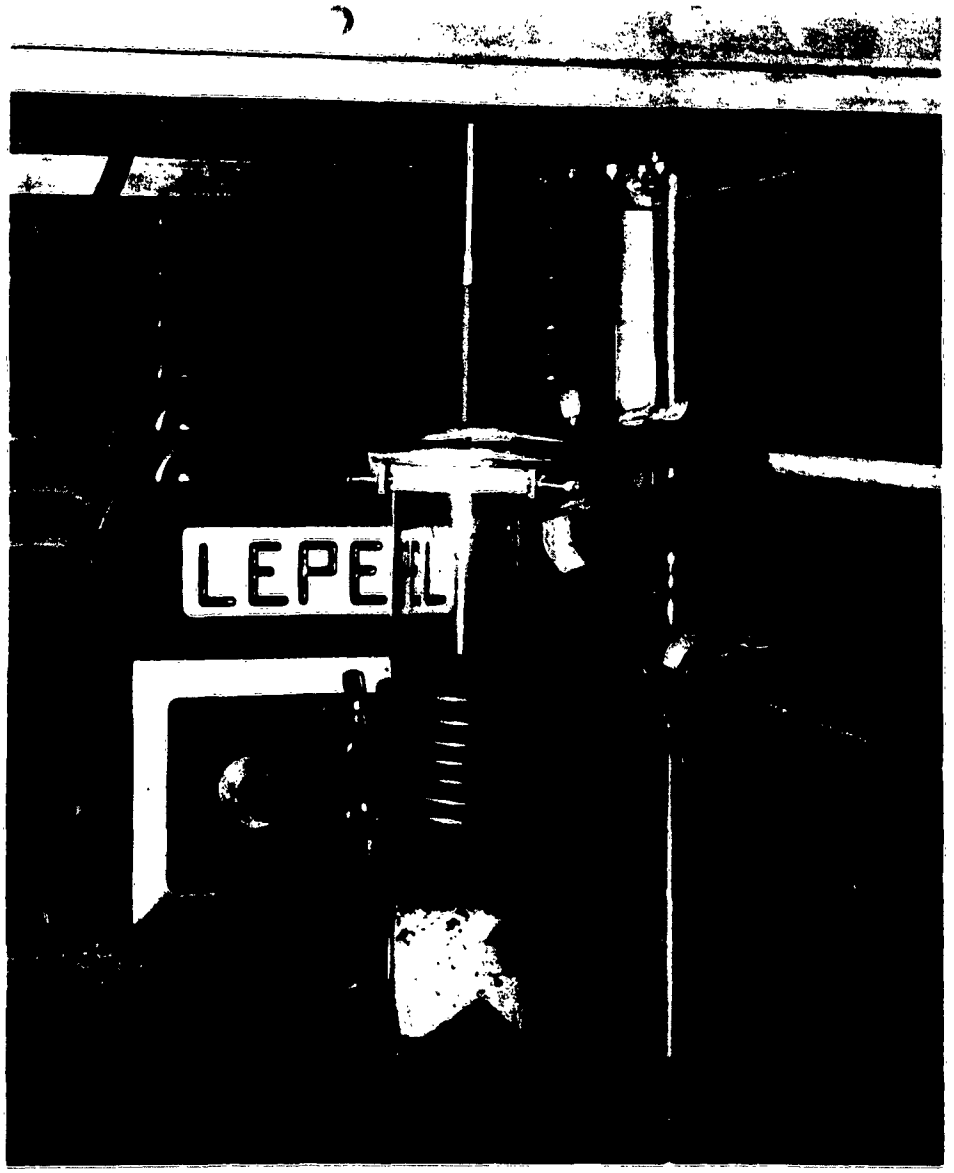


Figure 7
Fiber Drawing Unit

Fiber Unit Operation (Continued)

The assumption is made that if the temperature control and distribution were adequate, mechanical feed equipment would permit fibers to be drawn.

The tubing initially used was molybdenum and the life was limited. Tantalum tubing, used as part of the susceptor, has proven very satisfactory.

Induction Concentrator

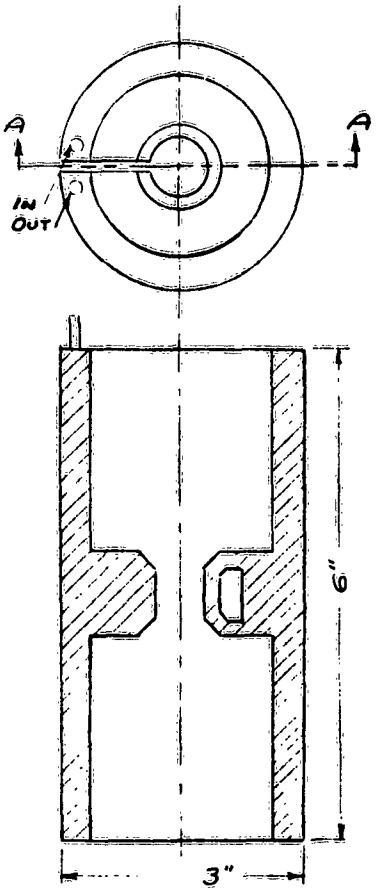
A field trip was made to the University of California at Berkeley to investigate the construction of an electron gun as a heat source. The use of an electron gun was discouraged in favor of induction heating with the use of a concentrator.

A diagram of the induction concentrator unit is shown in Figure 9. The sides are water cooled with emphasis on cooling in the center. The unit operated satisfactorily, heating only the narrow, center zone. This susceptor will be investigated further for both fiber work and other high temperature applications

Ceramic Fiber-Ceramic Matrix System

A laboratory setup for winding fiber-ceramic matrix test rings was fabricated as shown in Figure 10. The "E" glass roving was fed through an electric furnace at 800°F to remove sizing, passed through a colloidal silica suspension, and wound on a glass cylinder. The wrapping consisted of 16 threads per inch for two layers and then a longitudinal layer of 8 threads per inch. The wrapping was repeated to produce 1/8" thick rings of 3 inch diameter. The rings were dried for one hour at 212°F, removed from the cylinder, and fired for 10 minutes at 1200°F. The fired rings were dipped in the colloidal silica suspension and the drying and firing process repeated until a solid specimen was produced.

The test rings exhibited a degree of flexibility and "life" was left in the fibers. Additional perfection of techniques is required before any quantitative tests are believed to be in order.

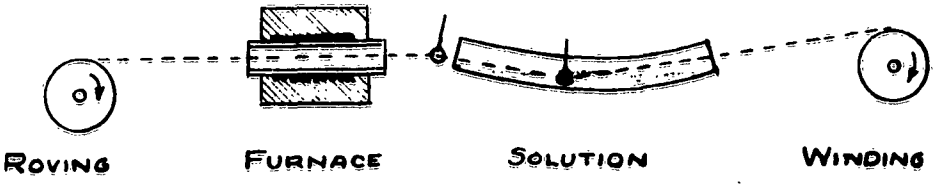


SECTION A-A

FIGURE 9
INDUCTION CONCENTRATOR

WATER FLOWS TO CENTER RING THEN THROUGH 6 VERTICAL PASSES NOT SHOWN

FIGURE 10
TEST RING FABRICATION UNIT



CONCLUSIONS:

The following items of a fundamental research nature require investigation before additional work is warranted.

1. The nature of the viscosity of glass and molten refractory oxides.
2. The composition limits to glass formation.
3. The effect of particle size on melting point.

This project progressed to the point of equipment limitations in production of fiber. Additional work can be performed on composite systems using existing fibers.

REFERENCES

1. Anderson, O.L., "Calculation of Activation Energy of Ionic Conductivity in Silica Glasses by Classical Methods", J. Am. Ceram. Soc. 37(12) 573-80 (1954).

2. Anderson, O.L. & Stuart, D.A., "Statistical Theories Applied to Glassy State", Ind. Eng. Chem. 46 (1) 1954-60 (1954).

3. Anderson, O.L., "Effect of Pressure on Glass Structure", J. Appl. Phys. 27(8) 943-49 (1956).

4. Babcock, C.L., "Coexisting Structures in Vitreous Silica", Ind. Eng. Chem. 46(1) 161-66 (1954).

5. Bikerman, J.J., "Surface Chemistry Theory and Applications", Academic Press Inc., New York, 1958.

6. Bockris, J.O.M., & Mackenzie, J.D., "Viscous Flow in Silica and Binary Liquid Silicates", Faraday Soc. Trans. 51 (July-Dec.) 1734-1747(1955)

7. Bockris, J.O.M., & Lowe, D.C., "Viscosity and Structure of Molten Silicates", Royal Society Proceedings, 226A (423-435) 1954.

8. Capps, W., "Viscosity of Glass", J. Colloid Sci. 7 (334-42) 1952.

9. Condon, E. V., "Physics of the Glassy State", Am. J. Physics, Part I Constitution and Structure 22(2) 43-53 (1954), Part II, Transformation Range 22(3) 132-42 (1954), Part III, Strength 22(4) 224-32 (1954), Part IV, Radiation Sensitive 22(5) 310-17 (1954).

10. Drummond, W. W., and Roth, W.P., "Research & Development on Fluidity Refractory Materials", NOrd - 18492, June 1959.

11. Fiedler, W. S.,"Quartz Fibers in High Temperature Resistant Materials", AFFDR TR-58-91, May 1958.

12. Forry, K. E., "2 Peaks in Internal Friction as Function of Temperature in Some Soda Silica Glasses", J. Am. Ceram. Soc. 40(3) 90-94(1957).

13. Galli, J. R., "Development and Evaluation of Rocket Blast and Rain Erosion Composite Coatings Produced by Flame Spray Techniques", WADC Tech. Report 58-493, February 1959.

14. Gibbs, J.H. and DiMarzio, E.A., "Nature of Glass Transition and the Glassy State", J. Chem. Phys. 28(3) 373-83 (1958).

15. Good, R. F., Private Communication

REFERENCES (Continued)

16. Glasstone, S., Laidler, K.J., & Eyring, H., "The Theory of Rate Processes", McGraW-Hill, New York, 1941.

17. Horizon's, Inc. Cleveland, Ohio, June 1959,

18. Huggins, M.L., "Structure of Glasses", J. Am. Ceram. Soc. 38(5) 172-75 (1955).

19. Kirby, P.L., "Some Aspects of the Viscoelasticity of Glass and Its Structure", J. Soc. Glass Tech 41(198) 95-116T (1957).

20. Kruh, R.F., "The Effect of Temperature Coefficient on Surface Tension of Molten Glasses", J. Chem. Phys. 27(1) 319-20 (1957).

21. Levengood, W.C., "Effect of Origin of Flow Characteristics on Glass Str.," J. Appl. Phys. 29(5) 820-26 (1958).

22. Levin, E.M. and Block, S., "Structural Interpretation of Immiscibility in Oxide Systems", J. Am. Ceram. Soc.
I Analysis and Calculation 40(3) 95 (1957)
II Coordination Principle Applied 40 (4) 113 (1957)
III Effect of Alkalis and Alumina 41(2) 49-54 (1958)
In Ternary Systems

23. Lyle, A.K., "Viscosity Data of Commerical Glass, Correlation with Working Characteristics", Ind. Eng. Chem. 46(1) 166-70 (1954)

24. Mackenzie, J.D., "The Physical Chemistry of Simple Molten Glasses", Chem. Review 56 (455-466) 1956.

25. Barboe, E.C., and Weyl, W.A., "Atomistic Interpretation of the Effect of Composition on the Viscosity of Glass", J. Soc. Glass Tech 39 (186) 16-368 (1955).

26. McKinnis, C.L., and Sutton, J.W., "The Glass Melting Process", J. Am. Ceram. Soc. (I) 42 (4)194(1959), (II) 42(5) 250 (1959).

27. Nelson, L.S., "Flash Heating - A New Technique", C & EN News 62, June 8, 1959.

28. Otto, W.H., "Properties of Glass Fibers at Elevated Temperatures", NOas 58-841-c, September 1958.

29. Prebus, A.F. and Michener, J.W., "Electron Microscope Investigation of Glass", Ind. & Engr. Chem. 46 (1) 147-153 (1954).

30. Sanyal, N.K. and Mitra, S.S., "Relation of Viscosity and Surface Tension of Liquids", J. Chem. Phys. 24 (2) 473 (1956).

REFERENCES (Continued)

31. Shoffner, J. E., "Ceramic Matrix-Ceramic Fiber Composite Systems", Convair-San Diego MP-58-148.2, January 1959.

32. Silver, A.H. and Bray, P.J., "Nuclear Magnetic Resonance Absorption in Glass. I. Nuclear Quadruple Effects in Boron Oxide, Soda-Boric Oxide, and Borosilicate Glasses", J. Chem. Phys. 29(5) 984-990 (1958).

33. Smythe, H., "Elastic Properties of Glasses", J. Am. Ceram. Soc. 42(6) 276-79 (1959).

34. Tiede, R. L., "Viscometer for Measurement of Glass Viscosity of Flow Through Orifices", J. Am. Ceram. Soc. 38(5) 183-86 (1955).

35. Warren, B.E., and Pincus, A. G., "Atomic Consideration of Immiscibility in Glass Systems", J. Am. Ceram. Soc. 23(10) 301-304 (1940).

36. Weik, H., "Observation on the Effect of Surface and Structure on the Tensile Strength of Iron Whiskers", WADC Tech Note 58-365, May 1959.

37. Winter, A., "Glass Formation", J. Am. Ceram. Soc., 40(2) 54-56 (1957).